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TITLE : SILVER ALLOY FOR REFLECTION FILM FOR OPTICAL RECORDING DISK

ABSTRACT : PROBLEM TO BE SOLVED: To provide a silver alloy for a reflection film having high thermal conductivity and suitable for an optical recording disk dealing with high recording density, by which high data reliability can be secured.

SOLUTION: The silver alloy consists essentially of Ag and contains at least one first added element of 0.001-0.1 wt.% selected from the group consisting of Cr, Zr, La, Ce, Eu, Ca, Sr, Ba, Ru, Ni and W. In the silver alloy for the reflection film, at least one second added element of 0.1-5 wt.% selected from the group consisting of Zn, Mg, Au and Pd can be added to the first added element.

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CLAIMS

[Claim(s)]

[Claim 1] A silver alloy for optical recording disk reflection films which uses Ag as the main ingredients and is characterized by the remainder consisting of inevitable impurities including Cr, Zr, La, Ce, Eu, Ca, Sr, Ba, Ru, nickel, and at least one sort of alloying elements chosen from a group which consists of W 0.001 to 0.1% of the weight.

[Claim 2] The silver alloy for optical recording disk reflection films according to claim 1 by which at least one sort of 2nd alloying elements chosen from a group which consists of Zn, Mg, Au, and Pd being included 0.1 to 5% of the weight in addition to said alloying element.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the silver alloy used as a reflection film of various optical recording disks.

[0002]

[Description of the Prior Art] As a medium which records computer information, video information, or music information, various optical recording disks (henceforth an optical disc), such as CD, CD-R, CD-RW, DVD, DVD-RW, DVD-RAM, MOD, and MD, are used.

[0003] As for these optical discs, the thin film which uses as a substrate a transparent disk [like polycarbonate] made from a plastic whose all are although structures differ, respectively, and has various functions, such as a reflection film and a protective film, on it is formed in layers by the method.

[0004] The reflection film of this optical disc has functions, such as missing the heat resulting from a laser beam with the function to reflect the laser beam used for reading and writing of record.

It is used for any optical disc of the method.

As construction material of this reflection film, aluminum, Au, Ag, or these alloys are mainly used.

[0005] These reflection films are formed of the usual sputtering process etc. using the target which consists of aluminum, Au, Ag, or these alloys.

[0006]

[Problem(s) to be Solved by the Invention] In recent years, the storage density of an optical disc follows on improving, and the demand of a thermally conductive high reflection film is increasing. However, about the reflection film of aluminum, it is clear from the point that thermal conductivity is low that demand characteristics cannot be satisfied. Although the reflection film of Au has a possibility that the demand characteristics about high heat conductivity can be satisfied, since the price is

dramatically high, it is difficult to use for a commercial optical disc.

[0007]On the other hand, about the reflection film of Ag, although thermal conductivity is satisfied, it has the problem of degradation of the characteristic by rewriting of data, the storage under a high-humidity/temperature environment, etc. being large, and being hard to secure the reliability of data. For this reason, the reflection film with which it is thoroughly satisfied of thermally conductive demand characteristics simultaneously is not obtained, securing the reliability of data.

[0008]Securing the reliability of high data in view of this conventional situation, this invention has high thermal conductivity simultaneously, and an object of this invention is to provide the silver alloy for reflection films suitable as an object for optical discs corresponding to high recording density.

[0009]

[Means for Solving the Problem]In order to attain the above-mentioned purpose, a silver alloy for reflection films of an optical recording disk which this invention provides, Ag is used as the main ingredients and the remainder consists of inevitable impurities, including Cr, Zr, La, Ce, Eu, Ca, Sr, Ba, Ru, nickel, and at least one sort of alloying elements chosen from a group which consists of W 0.001 to 0.1% of the weight.

[0010]In addition to said alloying element, in a silver alloy for optical recording disk reflection films of above-mentioned this invention, at least one sort of 2nd alloying elements chosen from a group which consists of Zn, Mg, Au, and Pd can be included 0.1 to 5% of the weight.

[0011]

[Embodiment of the Invention]As a result of examining various causes that the reflection film of the optical disc which consists of conventional pure Ag is inferior in the reliability of data, this invention persons checked that big-and-rough-izing of a crystal grain or membranous corrosion had the main causes, and found out that the alloying by addition of various elements was effective as the measure.

[0012]That is, in the silver alloy for reflection films of the optical disc of this invention, Cr, Zr, La, Ce, Eu, Ca, Sr, Ba, Ru, nickel, and at least one sort of alloying elements chosen from W are included 0.001 to 0.1% of the weight to Ag which is the main ingredients. By raising the heat resistance of a silver alloy, these alloying elements serve to suppress big and rough-ization of the crystal grain in a reflection film, and can obtain high reflectance now stably by the minuteness making of a crystal grain simultaneously. By including these alloying elements, minuteness making also of the crystal grain diameter of a target is carried out, and the effect that a sputtering rate is equalized is also acquired.

[0013]It is because the corrosion resistance of an alloy will fall and the characteristic degradation of the disk by rewriting etc. will occur, if having made the addition of these elements into 0.001 to 0.1 % of the weight in total has too low concentration at less than 0.001 % of the weight, and sufficient addition effect is not acquired but it exceeds 0.1 % of the weight conversely. Also when these alloying elements are added combining two or more sorts, it is possible to attain the desired characteristic, but the addition effect that the direction which generally crawls and adds a gap or one sort independently is obtained becomes large.

[0014]In addition to the 1st above-mentioned alloying element, at least one sort of 2nd alloying elements chosen from the group which consists of Zn, Mg, Au, and Pd can be

included 0.1 to 5% of the weight as the 2nd gestalt in the silver alloy for reflection films of the optical disc of this invention. In the case of an optical disc provided with the protective film which has the effect of raising corrosion resistance and contains especially ZnS, these 2nd alloying elements are effective.

[0015]It is because having made the addition of these 2nd alloying elements into 0.1 to 5 % of the weight has too low concentration at less than 0.1 % of the weight, and its effect of corrosion-resistant improvement is not enough, and the thermal conductivity of an alloy falls and it becomes impossible to correspond to high recording density-ization of an optical disc, when it exceeds 5 % of the weight conversely.

[0016]This invention can specify the presentation of the Ag alloy which constitutes a reflection film, and can be similarly specified about the presentation of the sputtering target used for formation of a reflection film.

[0017]The reflection film of the reflector whose high reflectance is [that the corrosion resistance else / for optical discs / is required] required for the reflection film of this invention, The use of the reflection film for lights, the reflection film for signs, the reflection film for reflectors, etc., Or heat dissipation nature is also applicable also to a use like reflection films, such as a liquid crystal display (LCD) which becomes important, a plasma display (PDP), and an electro MINESSENSU (EL) display, and also the use of various wiring materials with required electrical resistivity being small, etc.

[0018]

[Example]Ag, Cr, Zr which have 99.9 to 99.999% of purity as a raw material, The target of each sample was produced using the lump or powder of La, Ce, Eu, Ca, Sr, Ba, Ru, nickel, W, Zn, Mg, Au, and Pd with powder-metallurgy processing using the dissolution casting process or hotpress using a vacuum melting furnace. The presentation of the target in each obtained sample is shown in the following table 1.

[0019]

[Table 1]

試料	ターゲット組成(wt%)		ターゲット組成(at%)
	第1添加元素	第2添加元素	
1	0.001Zr	—	Ag99.999Zr0.001
2	0.001Ce	—	Ag99.999Ce0.001
3	0.001Ca	—	Ag99.997Ca0.003
4	0.001Ru	—	Ag99.999Ru0.001
5	0.001Sr	—	Ag99.999Sr0.001
6	0.001Ba	—	Ag99.999Ba0.001
7	0.01Cr	—	Ag99.979Cr0.021
8	0.01La	—	Ag99.992La0.008
9	0.1Eu	—	Ag99.929Eu0.071
10	0.1Zr	—	Ag99.882Zr0.118
11	0.1Ce	—	Ag99.923Ce0.077
12	0.1Ca	—	Ag99.781Ca0.269
13	0.1Ru	—	Ag99.808Ru0.107
14	0.001Ni	—	Ag99.998Ni0.002
15	0.1Ni	—	Ag99.816Ni0.184
16	0.001W	—	Ag99.999W0.001
17	0.1W	—	Ag99.941W0.059
18	0.01Ru	0.5Zn	Ag99.167Ru0.011Zn0.823
19	0.01Ce	5Zn	Ag92.000Ce0.008Zn7.992
20	0.01Zr	0.5Mg	Ag97.807Zr0.012Mg2.181
21	0.01Ca	5Mg	Ag81.049Ca0.023Mg18.929
22	0.1Cr	0.5Au	Ag99.518Cr0.274Au0.208
23	0.001Cr	5Au	Ag97.198Cr0.002Au2.802
24	0.1La	0.5Pd	Ag99.416La0.078Pd0.507
25	0.001La	5Pd	Ag94.934La0.001Pd5.066
26	0.01W	5Au	Ag97.192W0.006Au2.802
27	0.01Ni	5Pd	Ag94.916Ni0.018Pd5.066
28	0.1Sr	1Zn1Pd	Ag97.289Sr0.122Zn1.638Pd1.001
29	0.1Br	1Mg1Au	Ag95.082Ba0.076Mg4.310Au0.632
30	0.001Eu	2Pd2Au	Ag96.849Eu0.001Pd2.045Au1.105
31	0.1W	8Au2Zn	Ag94.993W0.059Zn3.303Au1.645
32	0.1Ni	1Mg4Pd	Ag91.625Ni0.177Mg4.284Pd3.914
33*	—	—	Ag
34*	0.3Cr	—	Ag99.38Cr0.62
35*	0.3La	—	Ag99.922La0.078
36*	0.1Ca	7Mg	Ag74.773Ca0.217Mg25.01
37*	0.1La	7Pd	Ag92.882La0.078Pd7.090

(注) 表中の*を付した試料は比較例である(以下同じ)。

[0020]The 3000-Å-thick thin film for characterization was formed on the glass substrate with magnetron sputtering method using each of these targets. It checked by the chemical analysis that the presentation of the formed thin film was almost equivalent to the used target presentation.

[0021]Reflectance, thermal conductivity, and crystal grain stability were evaluated using the obtained thin film. That is, about thermal conductivity, since it was difficult to measure the thermal conductivity of a thin film directly, it asked by calculating using a Wiedemann-Franz rule from the electrical resistance measured by the direct-current 4 terminal method, and the result was shown in the following table 2. With the spectrophotometer, measurement of reflectance was performed at the wavelength 400 and 650 or 780 nm, and showed the result in Table 3.

[0022]

[Table 2]

試料	反射膜	熱伝導率(W/m·K)
1	Ag99.999Zr0.001	298.80
2	Ag99.999Ce0.001	296.25
3	Ag99.997Ca0.003	295.24
4	Ag99.999Ru0.001	294.98
5	Ag99.999Sr0.001	296.95
6	Ag99.999Ba0.001	297.07
7	Ag99.979Cr0.021	294.03
8	Ag99.992La0.008	201.54
9	Ag99.929Eu0.071	273.75
10	Ag99.882Zr0.118	259.92
11	Ag99.923Ce0.077	285.01
12	Ag99.731Ca0.269	285.05
13	Ag99.898Ru0.107	273.71
14	Ag99.998Ni0.002	291.86
15	Ag99.816Ni0.184	249.02
16	Ag99.999W0.001	296.84
17	Ag99.941W0.059	290.59
18	Ag99.167Ru0.011Zn0.823	287.13
19	Ag92.000Ce0.008Zn7.992	96.74
20	Ag97.807Zr0.012Mg2.181	208.47
21	Ag81.049Ca0.023Mg18.929	72.43
22	Ag99.518Cr0.274Au0.208	229.44
23	Ag97.196Cr0.002Au2.802	203.74
24	Ag99.415La0.078Pd0.507	262.99
25	Ag94.934La0.001Pd5.066	156.16
26	Ag97.192W0.006Au2.802	205.62
27	Ag94.916Ni0.018Pd5.066	148.86
28	Ag97.239Sr0.122Zn1.638Pd1.001	188.63
29	Ag95.082Ba0.076Mg4.310Au0.532	165.14
30	Ag96.849Eu0.001Pd2.045Au1.105	192.70
31	Ag94.993W0.059Zn3.303Au1.645	139.81
32	Ag91.625Ni0.177Mg4.284Pd3.914	107.83
33*	Ag	297.55
34*	Ag99.38Cr0.62	169.10
35*	Ag99.922La0.078	285.72
36*	Ag74.778Ca0.217Mg25.01	58.14
37*	Ag92.832La0.078Pd7.090	129.21

[0023]

[Table 3]

材料	反射膜	反射率(%)		
		780(nm)	650(nm)	400(nm)
1	Ag99.999Zr0.001	97.9	97.7	94.2
2	Ag99.999Ce0.001	97.9	97.7	94.2
3	Ag99.997Ca0.008	97.9	97.7	94.2
4	Ag99.999Ru0.001	97.9	97.7	94.2
5	Ag99.999Sr0.001	97.9	97.7	94.2
6	Ag99.999Ba0.001	98.0	97.9	94.8
7	Ag99.979Cr0.021	97.5	97.3	94.5
8	Ag99.992La0.008	98.0	97.9	94.8
9	Ag99.929Eu0.071	98.0	97.9	94.8
10	Ag99.882Zr0.118	97.4	97.2	94.6
11	Ag99.923Ce0.077	98.0	97.0	94.8
12	Ag99.731Ca0.269	97.3	97.0	94.0
13	Ag99.893Ru0.107	97.4	97.1	94.0
14	Ag99.998Ni0.002	98.0	97.9	94.8
15	Ag99.816Ni0.184	97.9	97.7	94.3
16	Ag99.999W0.001	98.0	97.9	94.8
17	Ag99.941W0.059	98.0	97.9	94.8
18	Ag99.167Ru0.011Zn0.823	97.3	97.0	93.9
19	Ag92.000Ce0.008Zn7.992	90.2	89.9	85.9
20	Ag97.807Zr0.012Mg2.181	92.1	91.7	88.8
21	Ag81.049Ca0.023Mg18.929	80.9	79.0	65.3
22	Ag99.518Cr0.274Au0.208	97.4	97.2	94.4
23	Ag97.196Cr0.002Au2.802	91.9	90.1	88.2
24	Ag99.415La0.078Pd0.507	97.4	97.2	94.3
25	Ag94.934La0.001Pd5.066	90.3	89.9	86.0
26	Ag97.192W0.006Au2.802	91.8	90.2	88.3
27	Ag94.916Ni0.018Pd5.066	90.8	89.9	86.2
28	Ag97.239Sr0.122Zn1.638Pd1.001	91.6	90.1	88.5
29	Ag95.082Ba0.076Mg4.310Au0.532	90.7	89.9	86.1
30	Ag96.849Eu0.001Pd2.045Au1.105	91.3	89.8	88.3
31	Ag94.993W0.059Zn3.303Au1.645	90.2	89.8	85.7
32	Ag91.626Ni0.177Mg4.284Pd3.914	90.2	89.7	85.7
33*	Ag	98.0	97.9	94.8
34*	Ag99.38Cr0.62	97.5	97.2	94.1
35*	Ag99.922La0.078	98.0	97.9	94.8
36*	Ag74.773Ca0.217Mg25.01	74.9	71.3	63.4
37*	Ag92.882La0.078Pd7.090	91.2	89.9	87.8

[0024]Change of the crystal grain diameter before and after performing heat treatment of 48 hours at 150 ** in a high vacuum was investigated as an index showing the difficulty of happening of big-and-rough-izing of a crystal grain. The result evaluated by surface roughness (center-line-surface-roughness Ra) which measured the calculated value calculated from the X diffraction full width at half maximum with the following table 4 and an atomic force microscope as a crystal grain diameter before and behind heat treatment was shown in the following table 5. It is thought that a crystal grain diameter is large, so that surface roughness is large in the case of Table 5.

[0025]

[Table 4]

試料	反射膜	粒徑 L (111)[Å]	
		熱処理前	熱処理後
1	Ag99.999Zr0.001	175	170
2	Ag99.999Ce0.001	174	171
3	Ag99.997Ca0.003	176	170
4	Ag99.999Ru0.001	175	170
5	Ag99.999Sr0.001	175	171
6	Ag99.999Ba0.001	175	170
7	Ag99.979Cr0.021	176	173
8	Ag99.992La0.008	176	170
9	Ag99.929Eu0.071	175	170
10	Ag99.882Zr0.118	173	170
11	Ag99.923Ce0.077	174	170
12	Ag99.731Ca0.269	175	170
13	Ag99.893Ru0.107	175	170
14	Ag99.998Ni0.002	176	171
15	Ag99.816Ni0.184	175	170
16	Ag99.999W0.001	174	170
17	Ag99.941W0.059	175	170
18	Ag99.167Ru0.011Zn0.823	155	151
19	Ag92.000Ce0.008Zn7.992	155	155
20	Ag97.807Zr0.012Mg2.181	170	170
21	Ag81.049Ca0.023Mg18.929	170	170
22	Ag99.518Cr0.274Au0.208	160	160
23	Ag97.196Cr0.002Au2.802	160	160
24	Ag99.415La0.078Pd0.507	165	165
25	Ag94.934La0.001Pd5.066	165	165
26	Ag97.192W0.006Au2.802	160	160
27	Ag94.916Ni0.018Pd5.066	165	165
28	Ag97.239Sr0.122Zn1.638Pd1.001	150	150
29	Ag95.082Ba0.076Mg4.310Au0.532	150	150
30	Ag96.849Eu0.001Pd2.045Au1.105	145	145
31	Ag94.993W0.059Zn3.303Au1.645	145	145
32	Ag91.625Ni0.177Mg4.284Pd3.914	145	145
33*	Ag	165	175
34*	Ag99.38Cr0.62	175	193
35*	Ag99.922La0.078	175	180
36*	Ag74.773Ca0.217Mg25.01	165	165
37*	Ag92.832La0.078Pd7.090	165	165

[0026]

[Table 5]

試料	反射膜	表面粗さ R _a (Å)	
		熱処理前	熱処理後
1	Ag99.999Zr0.001	<10	<10
2	Ag99.999Ce0.001	<10	<10
3	Ag99.997Ca0.003	<10	<10
4	Ag99.999Ru0.001	<10	<10
5	Ag99.999Sr0.001	<10	<10
6	Ag99.999Ba0.001	<10	<10
7	Ag99.979Cr0.021	<10	<10
8	Ag99.992La0.008	<10	<10
9	Ag99.929Eu0.071	<10	<10
10	Ag99.882Zr0.118	<10	<10
11	Ag99.928Ce0.077	<10	<10
12	Ag99.731Ca0.269	<10	<10
13	Ag99.893Ru0.107	<10	<10
14	Ag99.998Ni0.002	<10	<10
15	Ag99.816Ni0.184	<10	<10
16	Ag99.999W0.001	<10	<10
17	Ag99.941W0.059	<10	<10
18	Ag99.167Ru0.011Zn0.823	<10	<10
19	Ag92.000Ce0.008Zn7.992	<10	<10
20	Ag97.807Zr0.012Mg2.181	<10	<10
21	Ag81.049Ca0.023Mg18.929	<10	<10
22	Ag99.518Cr0.274Au0.208	<10	<10
23	Ag97.196Cr0.002Au2.802	<10	<10
24	Ag99.415La0.078Pd0.507	<10	<10
25	Ag94.934La0.001Pd5.066	<10	<10
26	Ag97.192W0.006Au2.802	<10	<10
27	Ag94.916Ni0.018Pd5.066	<10	<10
28	Ag97.239Sr0.122Zn1.638Pd1.001	<10	<10
29	Ag95.082Ba0.076Mg4.310Au0.532	<10	<10
30	Ag96.849Eu0.001Pd2.045Au1.105	<10	<10
31	Ag94.993W0.059Zn3.303Au1.645	<10	<10
32	Ag91.625Ni0.177Mg4.284Pd3.914	<10	<10
33*	Ag	<10	23
34*	Ag99.38Cr0.62	10	11
35*	Ag99.922La0.078	10	10
36*	Ag74.773Ca0.217Mg25.01	<10	10
37*	Ag92.832La0.078Pd7.090	<10	10

[0027]Even if reflectance and thermal conductivity are high and it moreover receives heat from the above result by using the silver alloy of this invention, it turns out that the reflection film of the outstanding characteristic in which big and rough-ization of a crystal grain does not take place easily can be obtained.

[0028]Next, the disk characteristic at the time of using the reflection film of this invention for an optical disc was evaluated. That is, two kinds of substrates made from polycarbonate of the with 0.6 mm in thickness, 120 mm in diameter, the groove pitch of 0.8 micrometer, and a channel depth of 35 nm substrate for DVD were used as the substrate 1 as 1.2-mm [in thickness], 120-mm [in diameter], and slot (track) pitch 1.6micrometer, the substrate for CD with a channel depth of 50 nm, and the substrate 2.

[0029]The evaluation disk for CD was obtained by forming the overcoat layer of ultraviolet curing resin in a thickness of 5 micrometers, after forming a lower protective film, record film, an upper protective film, a diffusion preventing film, and a reflection film one by one by sputtering on the above-mentioned substrate 1. Similarly the

evaluation disk for DVD on the above-mentioned substrate 2 A lower protective film, After forming record film, an upper protective film, a diffusion preventing film, a reflection film, and a 4-micrometer-thick overcoat layer one by one, it produced by pasting together a polycarbonate board 0.6 mm in thickness, and 120 mm in diameter with ultraviolet curing resin on it. The thickness of the following table 7 and each film was shown for the composition of each disk sample which produced the sputtering condition used for film formation with the material of each of above-mentioned films to the following table 6 in the following table 8.

[0030]

[Table 6]

膜	材料系	投入電力 (kW)	ガス圧 (mTorr)	その他の条件
保護膜	ZnS+SiO ₂ 系	RF4.0	6	
拡散防止膜	SiNx	DC2.0	3	Siターゲット使用 N ₂ との反応スパッタ
	Ta ₂ O ₅	RF4.0	6	
	ZrO ₂	RF4.0	6	
	AlN	RF4.0	6	
	SiC	RF4.0	6	
記録膜	AgInSbTe系	DC0.5	3	
反射膜	Ag合金	DC1.0	3	

[0031]

[Table 7]

試料	反射膜	保護膜	拡散防止膜	基板
1	Ag99.999Zr0.001	(ZnS)80(SiO ₂)20	AlN	1
2	Ag99.999Ce0.001	(ZnS)80(SiO ₂)20	AlN	1
3	Ag99.997Ca0.003	(ZnS)80(SiO ₂)20	AlN	2
4	Ag99.999Ru0.001	(ZnS)80(SiO ₂)20	AlN	1
5	Ag99.999Sr0.001	(ZnS)80(SiO ₂)20	AlN	2
6	Ag99.999Ba0.001	(ZnS)80(SiO ₂)20	AlN	1
7	Ag99.979Cr0.021	(ZnS)80(SiO ₂)20	AlN	2
8	Ag99.992La0.008	(ZnS)80(SiO ₂)20	AlN	2
9	Ag99.929Eu0.071	(ZnS)80(SiO ₂)20	AlN	2
10	Ag99.882Zr0.118	(ZnS)80(SiO ₂)20	SiC	1
11	Ag99.923Ce0.077	(ZnS)80(SiO ₂)20	SiC	1
12	Ag99.791Ca0.269	(ZnS)80(SiO ₂)20	SiC	1
13	Ag99.893Ru0.107	(ZnS)80(SiO ₂)20	SiC	2
14	Ag99.998Ni0.002	(ZnS)80(SiO ₂)20	SiC	2
15	Ag99.816Ni0.184	(ZnS)80(SiO ₂)20	SiC	1
16	Ag99.999W0.001	(ZnS)80(SiO ₂)20	SiC	1
17	Ag99.941W0.059	(ZnS)80(SiO ₂)20	SiC	1
18	Ag99.167Ru0.011Zn0.823	(ZnS)80(SiO ₂)20	SiNx	2
19	Ag92.000Ce0.008Zn7.992	(ZnS)80(SiO ₂)20	—	2
20	Ag97.807Zr0.012Mg2.181	(ZnS)80(SiO ₂)20	Ta ₂ O ₅	2
21	Ag81.049Ca0.023Mg18.929	(ZnS)80(SiO ₂)20	—	2
22	Ag99.518Cr0.274Au0.208	(ZnS)80(SiO ₂)20	AlN	1
23	Ag97.196Cr0.002Au2.802	(ZnS)80(SiO ₂)20	SiNx	1
24	Ag99.415La0.078Pd0.507	(ZnS)80(SiO ₂)20	ZrO ₂	1
25	Ag94.934La0.001Pd5.066	(ZnS)80(SiO ₂)20	—	2
26	Ag97.192W0.006Au2.802	(ZnS)80(SiO ₂)20	—	2
27	Ag94.916Ni0.018Pd5.066	(ZnS)80(SiO ₂)20	—	2
28	Ag97.239Sr0.122Zn1.638Pd1.001	(ZnS)80(SiO ₂)20	—	1
29	Ag95.082Ba0.076Mg4.310Au0.532	(ZnS)80(SiO ₂)20	—	2
30	Ag96.849Eu0.001Pd2.045Au1.105	(ZnS)80(SiO ₂)20	—	1
31	Ag94.993W0.059Zn8.303Au1.645	(ZnS)80(SiO ₂)20	—	2
32	Ag91.625Ni0.177Mg4.284Pd3.914	(ZnS)80(SiO ₂)20	—	2
33*	Ag	(ZnS)80(SiO ₂)20	SiNx	1
34*	Ag99.38Cr0.62	(ZnS)80(SiO ₂)20	Ta ₂ O ₅	2
35*	Ag99.922La0.078	(ZnS)80(SiO ₂)20	SiC	2
36*	Ag74.773Ca0.217Mg25.01	(ZnS)80(SiO ₂)20	—	1
37*	Ag92.832La0.078Pd7.090	(ZnS)80(SiO ₂)20	—	2

[0032]

[Table 8]

試料	下部保護膜 (nm)	記録膜 (nm)	上部保護膜 (nm)	拡散防止膜 (nm)	反射膜 (nm)
1	85	17.5	35	5	100
2	85	17.5	34	5	100
3	80	17.0	25	5	160
4	85	17.5	35	5	120
5	80	17.0	25	5	160
6	87	17.5	34	5	120
7	79	17.0	25	5	160
8	80	17.0	26	5	160
9	81	17.0	25	5	160
10	84	17.5	35	5	100
11	86	17.5	34	5	120
12	85	17.5	35	5	100
13	80	17.0	25	5	160
14	80	17.0	25	5	160
15	84	17.5	36	5	100
16	85	17.5	34	5	100
17	85	17.5	34	5	100
18	80	17.0	25	5	170
19	80	17.0	25	—	170
20	80	17.0	25	5	170
21	80	17.0	25	—	160
22	85	17.5	35	5	100
23	85	17.5	34	5	120
24	85	17.5	34	5	110
25	80	17.0	25	—	160
26	80	17.0	25	—	160
27	80	17.0	25	—	160
28	85	17.5	34	—	100
29	80	17.0	25	—	160
30	85	17.5	34	—	100
31	80	17.0	25	—	160
32	80	17.0	25	—	160
33*	85	17.5	34	5	110
34*	79	17.0	27	5	170
35*	80	17.0	25	5	160
36*	85	17.5	35	—	100
37*	80	17.0	25	—	160

[0033]As evaluation of each disk obtained as mentioned above, a career versus the noise ratio (CNR), the jitter, and the modulation factor were measured. In the case of the evaluation disk for CD, it measured by narrowing down and irradiating the spot diameter of 1 micrometer with a laser beam with a wavelength of 780 nm through the lens of NA0.55. Linear velocity was made into 2.0 and 3 [5.0 or 10.0 m/sec] levels. In the case of the evaluation disk for DVD, it measured by narrowing down and irradiating the spot diameter of 0.5 micrometer with a laser beam with a wavelength of 633 nm through the lens of NA0.6. Linear velocity was made into 2 [7.0 or 15.0 m/sec] levels.

[0034]When laser power (power for Pe:elimination, Pw: power for writing) was fixed to Pe/Pw=0.5 with each linear velocity in any case and it changed Pw with 8-16 mW, CNR is large and the jitter measured by choosing the conditions which become and become small. The laser power of reading used 0.9 mW. Although the record film after film production was amorphous, the examination is presented where the whole disk surface is

crystallized by 10-mW DC light.

[0035] After keeping it to the high-humidity/temperature tub of 80 **85%RH for 500 hours in order to check the reliability of a disk, measurement of the disk characteristic was performed like the above. The disk characteristic of the back before high-humidity/temperature storage, i.e., CNR, the jitter, and the measurement result of the modulation factor were shown in the following table 9.

[0036]

[Table 9]

試料	反射膜組成(wt%)		ディスク特性					
	第1添加 元素	第2添加 元素	CNR(dB)		ジッター(%)		変調度(%)	
			前	後	前	後	前	後
1	0.001Zr	—	55.1	54.3	6.7	8.4	73.2	70.3
2	0.001Ce	—	55.0	54.8	6.9	8.3	72.1	69.3
3	0.001Ca	—	49.3	48.7	9.2	10.4	65.7	64.9
4	0.001Ru	—	54.3	53.8	6.6	8.4	69.2	69.0
5	0.001Sr	—	49.5	48.0	9.3	10.6	62.7	61.9
6	0.001Ba	—	54.8	54.0	7.1	8.0	71.3	70.1
7	0.01Cr	—	49.5	48.3	9.5	10.6	63.8	61.8
8	0.01La	—	49.2	48.1	10.3	11.2	64.3	62.0
9	0.1Eu	—	48.6	47.9	10.2	11.3	62.6	61.9
10	0.1Zr	—	56.2	54.9	7.7	8.9	68.2	66.3
11	0.1Ce	—	54.6	53.8	7.5	8.8	70.2	68.5
12	0.1Ca	—	53.0	52.6	7.4	8.6	68.5	67.2
13	0.1Ru	—	49.1	47.5	9.9	10.7	61.7	61.6
14	0.001Ni	—	49.5	48.2	10.4	11.3	63.9	61.3
15	0.1Ni	—	49.9	49.4	7.3	8.7	69.4	97.6
16	0.001W	—	55.9	54.9	6.9	8.1	72.7	70.0
17	0.1W	—	55.8	54.7	6.9	8.4	70.1	69.4
18	0.01Ru	0.5Zn	49.4	49.5	9.2	10.4	65.7	64.9
19	0.01Ce	5Zn	49.5	49.3	9.4	10.4	67.6	68.2
20	0.01Zr	0.5Mg	49.7	49.5	9.8	10.8	68.2	68.7
21	0.01Ca	5Mg	48.6	48.3	10.6	11.4	64.6	65.3
22	0.1Cr	0.5Au	55.1	53.9	6.9	8.1	74.4	74.3
23	0.001Cr	5Au	54.9	54.8	6.9	8.4	69.8	69.4
24	0.1La	0.5Pd	56.2	55.8	7.3	8.5	77.6	77.5
25	0.001La	5Pd	49.9	59.7	10.3	11.2	65.8	66.2
26	0.01W	5Au	50.1	49.9	10.3	11.2	66.5	66.9
27	0.01Ni	5Pd	50.0	49.6	9.2	10.4	73.7	76.9
28	0.1Sr	1Zn1Pd	54.4	53.7	6.8	8.4	76.9	75.5
29	0.1Br	1Mg1Au	48.8	47.9	9.9	10.3	64.7	62.4
30	0.001Eu	2Pd2Au	56.1	55.6	7.8	8.7	75.4	75.9
31	0.1W	3Au2Zn	48.2	47.1	9.7	10.4	62.4	60.9
32	0.1Ni	1Mg4Pd	49.2	47.3	9.3	10.5	63.2	61.9
33*	—	—	50.3	44.3	9.8	18.3	77.9	55.7
34*	0.3Cr	—	46.2	42.4	14.5	16.9	66.3	57.5
35*	0.3La	—	46.1	42.7	14.5	18.8	66.2	58.3
36*	0.1Ca	7Mg	50.1	44.2	9.8	18.6	75.9	55.4
37*	0.1La	7Pd	47.6	44.5	12.4	16.9	56.5	54.8

[0037] As for the reflection film using the silver alloy of this invention, it turns out that it not only has a good initial characteristic, but CNR, a jitter, and a modulation factor hardly deteriorate also after high-humidity/temperature storage, but it can obtain a reliable disk so that clearly from Table 9. On the other hand, since an initial characteristic with a good disk of the samples 33-37 which are comparative examples is not acquired, or either CRN, a jitter and a modulation factor deteriorate greatly after keeping it with high-humidity/temperature, it turns out that sufficient reliability is not securable.

[0038]The above result shows that especially the Ag alloy of this invention is suitable as a reflection film of an optical disc as an object for the optical discs of the next generation called for from now on. Although the reflection film was produced by sputtering process in the above-mentioned example, it can create also by various membrane formation art, such as various vacuum deposition methods, the ion plating method, various CVD methods, and the plating method.

[0039]

[Effect of the Invention]According to this invention, while it has high thermal conductivity, the reliability of high data can be secured and the silver alloy for reflection films suitable as an object for optical recording disks corresponding to high recording density can be provided.

TECHNICAL FIELD

[Field of the Invention]This invention relates to the silver alloy used as a reflection film of various optical recording disks.

PRIOR ART

[Description of the Prior Art]As a medium which records computer information, video information, or music information, various optical recording disks (henceforth an optical disc), such as CD, CD-R, CD-RW, DVD, DVD-RW, DVD-RAM, MOD, and MD, are used.

[0003]As for these optical discs, the thin film which uses as a substrate a transparent disk [like polycarbonate] made from a plastic whose all are although structures differ, respectively, and has various functions, such as a reflection film and a protective film, on it is formed in layers by the method.

[0004]The reflection film of this optical disc has functions, such as missing the heat resulting from a laser beam with the function to reflect the laser beam used for reading and writing of record.

It is used for any optical disc of the method.

As construction material of this reflection film, aluminum, Au, Ag, or these alloys are mainly used.

[0005]These reflection films are formed of the usual sputtering process etc. using the target which consists of aluminum, Au, Ag, or these alloys.

EFFECT OF THE INVENTION

[Effect of the Invention]According to this invention, while it has high thermal conductivity, the reliability of high data can be secured and the silver alloy for reflection films suitable as an object for optical recording disks corresponding to high recording density can be provided.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]In recent years, the storage density of an optical disc follows on improving, and the demand of a thermally conductive high reflection film is increasing. However, about the reflection film of aluminum, it is clear from the point that thermal conductivity is low that demand characteristics cannot be satisfied. Although the reflection film of Au has a possibility that the demand characteristics about high heat conductivity can be satisfied, since the price is dramatically high, it is difficult to use for a commercial optical disc.

[0007]On the other hand, about the reflection film of Ag, although thermal conductivity is satisfied, it has the problem of degradation of the characteristic by rewriting of data, the storage under a high-humidity/temperature environment, etc. being large, and being hard to secure the reliability of data. For this reason, the reflection film with which it is thoroughly satisfied of thermally conductive demand characteristics simultaneously is not obtained, securing the reliability of data.

[0008]Securing the reliability of high data in view of this conventional situation, this invention has high thermal conductivity simultaneously, and an object of this invention is to provide the silver alloy for reflection films suitable as an object for optical discs corresponding to high recording density.

MEANS

[Means for Solving the Problem]In order to attain the above-mentioned purpose, a silver alloy for reflection films of an optical recording disk which this invention provides, Ag is used as the main ingredients and the remainder consists of inevitable impurities, including Cr, Zr, La, Ce, Eu, Ca, Sr, Ba, Ru, nickel, and at least one sort of alloying elements chosen from a group which consists of W 0.001 to 0.1% of the weight.

[0010]In addition to said alloying element, in a silver alloy for optical recording disk reflection films of above-mentioned this invention, at least one sort of 2nd alloying elements chosen from a group which consists of Zn, Mg, Au, and Pd can be included 0.1 to 5% of the weight.

[0011]

[Embodiment of the Invention]As a result of examining various causes that the reflection film of the optical disc which consists of conventional pure Ag is inferior in the reliability of data, this invention persons checked that big-and-rough-izing of a crystal grain or membranous corrosion had the main causes, and found out that the alloying by addition of various elements was effective as the measure.

[0012]That is, in the silver alloy for reflection films of the optical disc of this invention, Cr, Zr, La, Ce, Eu, Ca, Sr, Ba, Ru, nickel, and at least one sort of alloying elements chosen from W are included 0.001 to 0.1% of the weight to Ag which is the main ingredients. By raising the heat resistance of a silver alloy, these alloying elements serve to suppress big and rough-ization of the crystal grain in a reflection film, and can obtain high reflectance now stably by the minuteness making of a crystal grain simultaneously. By including these alloying elements, minuteness making also of the crystal grain diameter of a target is carried out, and the effect that a sputtering rate is equalized is also

acquired.

[0013]It is because the corrosion resistance of an alloy will fall and the characteristic degradation of the disk by rewriting etc. will occur, if having made the addition of these elements into 0.001 to 0.1 % of the weight in total has too low concentration at less than 0.001 % of the weight, and sufficient addition effect is not acquired but it exceeds 0.1 % of the weight conversely. Also when these alloying elements are added combining two or more sorts, it is possible to attain the desired characteristic, but the addition effect that the direction which generally crawls and adds a gap or one sort independently is obtained becomes large.

[0014]In addition to the 1st above-mentioned alloying element, at least one sort of 2nd alloying elements chosen from the group which consists of Zn, Mg, Au, and Pd can be included 0.1 to 5% of the weight as the 2nd gestalt in the silver alloy for reflection films of the optical disc of this invention. In the case of an optical disc provided with the protective film which has the effect of raising corrosion resistance and contains especially ZnS, these 2nd alloying elements are effective.

[0015]It is because having made the addition of these 2nd alloying elements into 0.1 to 5 % of the weight has too low concentration at less than 0.1 % of the weight, and its effect of corrosion-resistant improvement is not enough, and the thermal conductivity of an alloy falls and it becomes impossible to correspond to high recording density-ization of an optical disc, when it exceeds 5 % of the weight conversely.

[0016]This invention can specify the presentation of the Ag alloy which constitutes a reflection film, and can be similarly specified about the presentation of the sputtering target used for formation of a reflection film.

[0017]The reflection film of the reflector whose high reflectance is [that the corrosion resistance else / for optical discs / is required] required for the reflection film of this invention, The use of the reflection film for lights, the reflection film for signs, the reflection film for reflectors, etc., Or heat dissipation nature is also applicable also to a use like reflection films, such as a liquid crystal display (LCD) which becomes important, a plasma display (PDP), and an electro MINESSENSU (EL) display, and also the use of various wiring materials with required electrical resistivity being small, etc.

EXAMPLE

[Example]Ag, Cr, Zr which have 99.9 to 99.999% of purity as a raw material, The target of each sample was produced using the lump or powder of La, Ce, Eu, Ca, Sr, Ba, Ru, nickel, W, Zn, Mg, Au, and Pd with powder-metallurgy processing using the dissolution casting process or hotpress using a vacuum melting furnace. The presentation of the target in each obtained sample is shown in the following table 1.

[0019]

[Table 1]

試料	ターゲット組成 (wt%)		ターゲット組成 (at%)
	第 1 添加元素	第 2 添加元素	
1	0.001Zr	—	Ag99.999Zr0.001
2	0.001Ce	—	Ag99.999Ce0.001
3	0.001Ca	—	Ag99.997Ca0.003
4	0.001Ru	—	Ag99.999Ru0.001
5	0.001Sr	—	Ag99.999Sr0.001
6	0.001Ba	—	Ag99.999Ba0.001
7	0.01Cr	—	Ag99.979Cr0.021
8	0.01La	—	Ag99.992La0.008
9	0.1Eu	—	Ag99.929Eu0.071
10	0.1Zr	—	Ag99.882Zr0.118
11	0.1Ce	—	Ag99.923Ce0.077
12	0.1Ca	—	Ag99.781Ca0.269
13	0.1Ru	—	Ag99.898Ru0.107
14	0.001Ni	—	Ag99.998Ni0.002
15	0.1Ni	—	Ag99.816Ni0.184
16	0.001W	—	Ag99.999W0.001
17	0.1W	—	Ag99.941W0.059
18	0.01Ru	0.5Zn	Ag99.167Ru0.011Zn0.823
19	0.01Ce	5Zn	Ag92.000Ce0.008Zn7.992
20	0.01Zr	0.5Mg	Ag97.807Zr0.012Mg2.181
21	0.01Ca	5Mg	Ag81.049Ca0.023Mg18.929
22	0.1Cr	0.5Au	Ag99.518Cr0.274Au0.208
23	0.001Cr	5Au	Ag97.196Cr0.002Au2.802
24	0.1La	0.5Pd	Ag99.415La0.078Pd0.507
25	0.001La	5Pd	Ag94.934La0.001Pd5.066
26	0.01W	5Au	Ag97.192W0.006Au2.802
27	0.01Ni	5Pd	Ag94.916Ni0.018Pd5.066
28	0.1Sr	1Zn1Pd	Ag97.239Sr0.122Zn1.638Pd1.001
29	0.1Br	1Mg1Au	Ag95.082Ba0.076Mg4.310Au0.532
30	0.001Eu	2Pd2Au	Ag96.849Eu0.001Pd2.046Au1.105
31	0.1W	8Au2Zn	Ag94.998W0.059Zn8.303Au1.645
32	0.1Ni	1Mg4Pd	Ag91.625Ni0.177Mg4.284Pd3.914
33*	—	—	Ag
34*	0.3Cr	—	Ag99.38Cr0.62
35*	0.3La	—	Ag99.922La0.078
36*	0.1Ca	7Mg	Ag74.773Ca0.217Mg25.01
37*	0.1La	7Pd	Ag92.882La0.078Pd7.090

(注) 表中の*を付した試料は比較例である (以下同じ)。

[0020]The 3000-Å-thick thin film for characterization was formed on the glass substrate with magnetron sputtering method using each of these targets. It checked by the chemical analysis that the presentation of the formed thin film was almost equivalent to the used target presentation.

[0021]Reflectance, thermal conductivity, and crystal grain stability were evaluated using the obtained thin film. That is, about thermal conductivity, since it was difficult to measure the thermal conductivity of a thin film directly, it asked by calculating using a Wiedemann-Franz rule from the electrical resistance measured by the direct-current 4 terminal method, and the result was shown in the following table 2. With the spectrophotometer, measurement of reflectance was performed at the wavelength 400 and 650 or 780 nm, and showed the result in Table 3.

[0022]

[Table 2]

試料	反射膜	熱伝導率(W/m・K)
1	Ag99.999Zr0.001	293.80
2	Ag99.999Ce0.001	296.25
3	Ag99.997Ca0.003	295.24
4	Ag99.999Ru0.001	294.98
5	Ag99.999Sr0.001	296.95
6	Ag99.999Ba0.001	297.07
7	Ag99.979Cr0.021	294.03
8	Ag99.992La0.008	201.54
9	Ag99.929Eu0.071	273.75
10	Ag99.882Zr0.118	259.92
11	Ag99.923Co0.077	285.01
12	Ag99.731Ca0.269	285.05
13	Ag99.898Ru0.107	273.71
14	Ag99.998Ni0.002	291.86
15	Ag99.816Ni0.184	240.02
16	Ag99.999W0.001	296.84
17	Ag99.941W0.059	290.59
18	Ag99.167Ru0.011Zn0.823	287.13
19	Ag92.000Ce0.008Zn7.992	96.74
20	Ag97.807Zr0.012Mg2.181	208.47
21	Ag81.049Ca0.023Mg18.929	72.43
22	Ag89.518Cr0.274Au0.208	229.44
23	Ag97.196Cr0.002Au2.802	203.74
24	Ag99.415La0.078Pd0.507	262.99
25	Ag94.934La0.001Pd5.066	156.16
26	Ag97.192W0.006Au2.802	205.62
27	Ag94.916Ni0.018Pd5.066	148.86
28	Ag97.239Sr0.122Zn1.638Pd1.001	183.63
29	Ag95.082Ba0.076Mg4.810Au0.532	165.14
30	Ag96.849Eu0.001Pd2.045Au1.105	192.70
31	Ag94.993W0.059Zn3.303Au1.645	189.81
32	Ag91.625Ni0.177Mg4.284Pd3.914	107.83
33*	Ag	297.55
34*	Ag99.38Cr0.62	169.10
35*	Ag99.922La0.078	285.72
36*	Ag74.778Ca0.217Mg25.01	58.14
37*	Ag92.832La0.078Pd7.090	129.21

[0023]

[Table 3]

試料	反射膜	反射率(%)		
		780(nm)	650(nm)	400(nm)
1	Ag99.999Zr0.001	97.9	97.7	94.2
2	Ag99.999Co0.001	97.9	97.7	94.2
3	Ag99.997Ca0.003	97.9	97.7	94.2
4	Ag99.999Ru0.001	97.9	97.7	94.2
5	Ag99.999Sr0.001	97.9	97.7	94.2
6	Ag99.999Ba0.001	98.0	97.9	94.8
7	Ag99.979Cr0.021	97.5	97.8	94.5
8	Ag99.992La0.008	98.0	97.9	94.8
9	Ag99.929Eu0.071	98.0	97.9	94.8
10	Ag99.882Zr0.118	97.4	97.2	94.6
11	Ag99.923Co0.077	98.0	97.0	94.8
12	Ag99.731Ca0.269	97.3	97.0	94.0
13	Ag99.893Ru0.107	97.4	97.1	94.0
14	Ag99.998Ni0.002	98.0	97.9	94.8
15	Ag99.816Ni0.184	97.9	97.7	94.3
16	Ag99.999W0.001	98.0	97.9	94.8
17	Ag99.941W0.059	98.0	97.9	94.8
18	Ag99.167Ru0.011Zn0.823	97.8	97.0	93.9
19	Ag92.000Co0.008Zn7.992	90.2	89.9	85.9
20	Ag97.807Zr0.012Mg2.181	92.1	91.7	88.8
21	Ag81.049Ca0.023Mg18.929	80.9	79.0	65.3
22	Ag99.518Cr0.274Au0.208	97.4	97.2	94.4
23	Ag97.196Cr0.002Au2.802	91.9	90.1	88.2
24	Ag99.415La0.078Pd0.507	97.4	97.2	94.3
25	Ag94.934La0.001Pd5.066	90.3	89.9	86.0
26	Ag97.192W0.006Au2.802	91.8	90.2	88.3
27	Ag94.916Ni0.018Pd5.066	90.8	89.9	86.2
28	Ag97.239Sr0.122Zn1.638Pd1.001	91.6	90.1	88.5
29	Ag95.082Ba0.076Mg4.310Au0.532	90.7	89.9	86.1
30	Ag96.849Eu0.001Pd2.045Au1.105	91.3	89.8	88.3
31	Ag94.993W0.059Zn3.303Au1.645	90.2	89.8	85.7
32	Ag91.625Ni0.177Mg4.284Pd3.914	90.2	89.7	85.7
33*	Ag	98.0	97.9	94.8
34*	Ag99.38Cr0.62	97.5	97.2	94.1
35*	Ag99.922La0.078	98.0	97.9	94.8
36*	Ag74.773Ca0.217Mg25.01	74.9	71.3	63.4
37*	Ag92.882La0.078Pd7.090	91.2	89.9	87.8

[0024]Change of the crystal grain diameter before and after performing heat treatment of 48 hours at 150 ** in a high vacuum was investigated as an index showing the difficulty of happening of big-and-rough-izing of a crystal grain. The result evaluated by surface roughness (center-line-surface-roughness Ra) which measured the calculated value calculated from the X diffraction full width at half maximum with the following table 4 and an atomic force microscope as a crystal grain diameter before and behind heat treatment was shown in the following table 5. It is thought that a crystal grain diameter is large, so that surface roughness is large in the case of Table 5.

[0025]

Table 4]

試料	反射膜	粒径 L (111)[Å]	
		熱処理前	熱処理後
1	Ag99.999Zr0.001	175	170
2	Ag99.999Ce0.001	174	171
3	Ag99.997Ca0.003	176	170
4	Ag99.999Ru0.001	175	170
5	Ag99.999Sr0.001	175	171
6	Ag99.999Ba0.001	175	170
7	Ag99.979Cr0.021	176	173
8	Ag99.992La0.008	176	170
9	Ag99.929Eu0.071	175	170
10	Ag99.882Zr0.118	173	170
11	Ag99.923Ce0.077	174	170
12	Ag99.731Ca0.269	175	170
13	Ag99.893Ru0.107	175	170
14	Ag99.998Ni0.002	176	171
15	Ag99.816Ni0.184	175	170
16	Ag99.999W0.001	174	170
17	Ag99.941W0.059	175	170
18	Ag99.167Ru0.011Zn0.823	155	151
19	Ag92.000Ce0.008Zn7.992	155	155
20	Ag97.807Zr0.012Mg2.181	170	170
21	Ag81.049Ca0.023Mg18.929	170	170
22	Ag99.518Cr0.274Au0.208	160	160
23	Ag97.196Cr0.002Au2.802	160	160
24	Ag99.415La0.078Pd0.507	165	165
25	Ag94.934La0.001Pd5.068	165	165
26	Ag97.192W0.006Au2.802	160	160
27	Ag94.916Ni0.018Pd5.066	165	165
28	Ag97.239Sr0.122Zn1.638Pd1.001	150	150
29	Ag95.082Ba0.076Mg4.310Au0.532	150	150
30	Ag96.849Eu0.001Pd2.045Au1.105	145	145
31	Ag94.993W0.059Zn3.303Au1.645	145	145
32	Ag91.625Ni0.177Mg4.284Pd3.914	145	145
33*	Ag	165	175
34*	Ag99.38Cr0.62	175	193
35*	Ag99.922La0.078	175	180
36*	Ag74.773Ca0.217Mg25.01	165	165
37*	Ag92.832La0.078Pd7.090	165	165

[0026]

[Table 5]

試料	反射膜	表面粗さ R _a (Å)	
		熱処理前	熱処理後
1	Ag99.999Zr0.001	<10	<10
2	Ag99.999Ce0.001	<10	<10
8	Ag99.997Ca0.003	<10	<10
4	Ag99.999Ru0.001	<10	<10
5	Ag99.999Sr0.001	<10	<10
6	Ag99.999Ba0.001	<10	<10
7	Ag99.979Cr0.021	<10	<10
8	Ag99.992La0.008	<10	<10
9	Ag99.929Eu0.071	<10	<10
10	Ag99.882Zr0.118	<10	<10
11	Ag99.923Ce0.077	<10	<10
12	Ag99.731Ca0.269	<10	<10
13	Ag99.893Ru0.107	<10	<10
14	Ag99.998Ni0.002	<10	<10
15	Ag99.816Ni0.184	<10	<10
16	Ag99.999W0.001	<10	<10
17	Ag99.941W0.059	<10	<10
18	Ag99.167Ru0.011Zn0.823	<10	<10
19	Ag92.000Ce0.008Zn7.992	<10	<10
20	Ag97.807Zr0.012Mg2.181	<10	<10
21	Ag81.049Ca0.023Mg18.929	<10	<10
22	Ag99.518Cr0.274Au0.208	<10	<10
23	Ag97.196Cr0.002Au2.802	<10	<10
24	Ag99.415La0.078Pd0.507	<10	<10
25	Ag94.934La0.001Pd5.066	<10	<10
26	Ag97.192W0.006Au2.802	<10	<10
27	Ag94.916Ni0.018Pd5.066	<10	<10
28	Ag97.239Sr0.122Zn1.638Pd1.001	<10	<10
29	Ag95.082Ba0.076Mg4.310Au0.532	<10	<10
30	Ag96.849Eu0.001Pd2.046Au1.105	<10	<10
31	Ag94.993W0.059Zn3.303Au1.645	<10	<10
32	Ag91.625Ni0.177Mg4.284Pd3.914	<10	<10
33*	Ag	<10	23
34*	Ag99.38Cr0.62	10	11
35*	Ag99.922La0.078	10	10
36*	Ag74.773Ca0.217Mg25.01	<10	10
37*	Ag92.832La0.078Pd7.090	<10	10

[0027] Even if reflectance and thermal conductivity are high and it moreover receives heat from the above result by using the silver alloy of this invention, it turns out that the reflection film of the outstanding characteristic in which big and rough-ization of a crystal grain does not take place easily can be obtained.

[0028] Next, the disk characteristic at the time of using the reflection film of this invention for an optical disc was evaluated. That is, two kinds of substrates made from polycarbonate of the with 0.6 mm in thickness, 120 mm in diameter, the groove pitch of 0.8 micrometer, and a channel depth of 35 nm substrate for DVD were used as the substrate 1 as 1.2-mm [in thickness], 120-mm [in diameter], and slot (track) pitch 1.6micrometer, the substrate for CD with a channel depth of 50 nm, and the substrate 2.

[0029] The evaluation disk for CD was obtained by forming the overcoat layer of ultraviolet curing resin in a thickness of 5 micrometers, after forming a lower protective film, record film, an upper protective film, a diffusion preventing film, and a reflection film one by one by sputtering on the above-mentioned substrate 1. Similarly the

evaluation disk for DVD on the above-mentioned substrate 2 A lower protective film, After forming record film, an upper protective film, a diffusion preventing film, a reflection film, and a 4-micrometer-thick overcoat layer one by one, it produced by pasting together a polycarbonate board 0.6 mm in thickness, and 120 mm in diameter with ultraviolet curing resin on it. The thickness of the following table 7 and each film was shown for the composition of each disk sample which produced the sputtering condition used for film formation with the material of each of above-mentioned films to the following table 6 in the following table 8.

[0030]

[Table 6]

膜	材料系	投入電力 (kW)	ガス圧 (mTorr)	その他の条件
保護膜	ZnS+SiO ₂ 系	RF4.0	6	
拡散防止膜	SiNx	DC2.0	3	Siターゲット使用 N ₂ との反応スパッタ
	Ta ₂ O ₅	RF4.0	6	
	ZrO ₂	RF4.0	6	
	AlN	RF4.0	6	
	SiC	RF4.0	6	
記録膜	AgInSbTe系	DC0.5	3	
反射膜	Ag合金	DC1.0	3	

[0031]

[Table 7]

試料	反射膜	保護膜	拡散防止膜	基板
1	Ag99.999Zr0.001	(ZnS)80(SiO ₂)20	AlN	1
2	Ag99.999Ce0.001	(ZnS)80(SiO ₂)20	AlN	1
3	Ag99.997Ca0.003	(ZnS)80(SiO ₂)20	AlN	2
4	Ag99.999Ru0.001	(ZnS)80(SiO ₂)20	AlN	1
5	Ag99.999Sr0.001	(ZnS)80(SiO ₂)20	AlN	2
6	Ag99.999Ba0.001	(ZnS)80(SiO ₂)20	AlN	1
7	Ag99.979Cr0.021	(ZnS)80(SiO ₂)20	AlN	2
8	Ag99.992La0.008	(ZnS)80(SiO ₂)20	AlN	2
9	Ag99.929Eu0.071	(ZnS)80(SiO ₂)20	AlN	2
10	Ag99.882Zr0.118	(ZnS)80(SiO ₂)20	SiC	1
11	Ag99.923Ce0.077	(ZnS)80(SiO ₂)20	SiC	1
12	Ag99.781Ca0.269	(ZnS)80(SiO ₂)20	SiC	1
13	Ag99.893Ru0.107	(ZnS)80(SiO ₂)20	SiC	2
14	Ag99.998Ni0.002	(ZnS)80(SiO ₂)20	SiC	2
15	Ag99.816Ni0.184	(ZnS)80(SiO ₂)20	SiC	1
16	Ag99.999W0.001	(ZnS)80(SiO ₂)20	SiC	1
17	Ag99.941W0.059	(ZnS)80(SiO ₂)20	SiC	1
18	Ag99.167Ru0.011Zn0.823	(ZnS)80(SiO ₂)20	SiNx	2
19	Ag92.000Ce0.008Zn7.992	(ZnS)80(SiO ₂)20	—	2
20	Ag97.807Zr0.012Mg2.181	(ZnS)80(SiO ₂)20	Ta ₂ O ₅	2
21	Ag81.049Ca0.023Mg18.929	(ZnS)80(SiO ₂)20	—	2
22	Ag99.518Cr0.274Au0.208	(ZnS)80(SiO ₂)20	AlN	1
23	Ag97.196Cr0.002Au2.802	(ZnS)80(SiO ₂)20	SiNx	1
24	Ag99.415La0.078Pd0.507	(ZnS)80(SiO ₂)20	ZrO ₂	1
25	Ag94.934La0.001Pd5.066	(ZnS)80(SiO ₂)20	—	2
26	Ag97.192W0.006Au2.802	(ZnS)80(SiO ₂)20	—	2
27	Ag94.916Ni0.018Pd5.066	(ZnS)80(SiO ₂)20	—	2
28	Ag97.239Sr0.122Zn1.638Pd1.001	(ZnS)80(SiO ₂)20	—	1
29	Ag95.082Ba0.076Mg4.310Au0.532	(ZnS)80(SiO ₂)20	—	2
30	Ag96.849Eu0.001Pd2.045Au1.105	(ZnS)80(SiO ₂)20	—	1
31	Ag94.993W0.059Zn8.303Au1.645	(ZnS)80(SiO ₂)20	—	2
32	Ag91.625Ni0.177Mg4.284Pd3.914	(ZnS)80(SiO ₂)20	—	2
33*	Ag	(ZnS)80(SiO ₂)20	SiNx	1
34*	Ag99.38Cr0.62	(ZnS)80(SiO ₂)20	Ta ₂ O ₅	2
35*	Ag99.922La0.078	(ZnS)80(SiO ₂)20	SiC	2
36*	Ag74.773Ca0.217Mg25.01	(ZnS)80(SiO ₂)20	—	1
37*	Ag92.832La0.078Pd7.090	(ZnS)80(SiO ₂)20	—	2

[0032]

[Table 8]

試料	下部保護膜 (nm)	記録膜 (nm)	上部保護膜 (nm)	拡散防止膜 (nm)	反射膜 (nm)
1	85	17.5	35	5	100
2	85	17.5	34	5	100
3	80	17.0	25	5	160
4	85	17.5	35	5	120
5	80	17.0	25	5	160
6	87	17.5	34	5	120
7	79	17.0	25	5	160
8	80	17.0	26	5	160
9	81	17.0	25	5	160
10	84	17.5	35	5	100
11	86	17.5	34	5	120
12	85	17.5	35	5	100
13	80	17.0	25	5	160
14	80	17.0	25	5	160
15	84	17.5	36	5	100
16	85	17.5	34	5	100
17	85	17.5	34	5	100
18	80	17.0	25	5	170
19	80	17.0	25	—	170
20	80	17.0	25	5	170
21	80	17.0	25	—	160
22	85	17.5	35	5	100
23	85	17.5	34	5	120
24	85	17.5	34	5	110
25	80	17.0	25	—	160
26	80	17.0	25	—	160
27	80	17.0	25	—	160
28	85	17.5	34	—	100
29	80	17.0	25	—	160
30	85	17.5	34	—	100
31	80	17.0	25	—	160
32	80	17.0	25	—	160
33*	85	17.5	34	5	110
34*	79	17.0	27	5	170
35*	80	17.0	25	5	160
36*	85	17.5	35	—	100
37*	80	17.0	25	—	160

[0033]As evaluation of each disk obtained as mentioned above, a career versus the noise ratio (CNR), the jitter, and the modulation factor were measured. In the case of the evaluation disk for CD, it measured by narrowing down and irradiating the spot diameter of 1 micrometer with a laser beam with a wavelength of 780 nm through the lens of NA0.55. Linear velocity was made into 2.0 and 3 [5.0 or 10.0 m/sec] levels. In the case of the evaluation disk for DVD, it measured by narrowing down and irradiating the spot diameter of 0.5 micrometer with a laser beam with a wavelength of 633 nm through the lens of NA0.6. Linear velocity was made into 2 [7.0 or 15.0 m/sec] levels.

[0034]When laser power (power for Pe:elimination, Pw: power for writing) was fixed to $P_e/P_w=0.5$ with each linear velocity in any case and it changed Pw with 8-16 mW, CNR is large and the jitter measured by choosing the conditions which become and become small. The laser power of reading used 0.9 mW. Although the record film after film production was amorphous, the examination is presented where the whole disk surface is

crystallized by 10-mW DC light.

[0035]After keeping it to the high-humidity/temperature tub of 80 **85%RH for 500 hours in order to check the reliability of a disk, measurement of the disk characteristic was performed like the above. The disk characteristic of the back before high-humidity/temperature storage, i.e., CNR, the jitter, and the measurement result of the modulation factor were shown in the following table 9.

[0036]

[Table 9]

試料	反射膜組成(wt%)		ディスク特性					
	第1添加元素	第2添加元素	CNR(dB)		ジッター(%)		変調度(%)	
			前	後	前	後	前	後
1	0.001Zr	—	55.1	54.8	6.7	8.4	73.2	70.3
2	0.001Ce	—	55.0	54.8	6.9	8.3	72.1	69.3
3	0.001Ca	—	49.3	48.7	9.2	10.4	65.7	64.9
4	0.001Ru	—	54.8	53.8	6.6	8.4	69.2	69.0
5	0.001Sr	—	49.5	48.0	9.3	10.5	62.7	61.9
6	0.001Ba	—	54.8	54.0	7.1	8.0	71.3	70.1
7	0.01Cr	—	49.5	48.3	9.5	10.6	63.8	61.8
8	0.01La	—	49.2	48.1	10.3	11.2	64.3	62.0
9	0.1Eu	—	48.6	47.9	10.2	11.3	62.6	61.9
10	0.1Zr	—	56.2	54.9	7.7	8.9	68.2	66.3
11	0.1Ce	—	54.6	53.8	7.5	8.8	70.2	68.5
12	0.1Ca	—	53.0	52.6	7.4	8.5	68.5	67.2
13	0.1Ru	—	49.1	47.5	9.9	10.7	61.7	61.6
14	0.001Ni	—	49.5	48.2	10.4	11.3	63.9	61.3
15	0.1Ni	—	49.9	49.4	7.8	8.7	69.4	97.6
16	0.001W	—	55.9	54.9	6.9	8.1	72.7	70.0
17	0.1W	—	55.8	54.7	6.9	8.4	70.1	69.4
18	0.01Ru	0.5Zn	49.4	49.5	9.2	10.4	65.7	64.9
19	0.01Ce	5Zn	49.5	49.3	9.4	10.4	67.6	68.2
20	0.01Zr	0.5Mg	49.7	49.5	9.8	10.8	68.2	68.7
21	0.01Ca	5Mg	48.6	48.3	10.5	11.4	64.6	65.3
22	0.1Cr	0.5Au	55.1	53.9	6.9	8.1	74.4	74.3
23	0.001Cr	5Au	54.9	54.8	6.9	8.4	69.8	69.4
24	0.1La	0.5Pd	56.2	55.8	7.3	8.5	77.6	77.5
25	0.001La	5Pd	49.9	59.7	10.3	11.2	65.8	66.2
26	0.01W	5Au	50.1	49.9	10.3	11.2	66.5	66.9
27	0.01Ni	5Pd	50.0	49.6	9.2	10.4	73.7	76.9
28	0.1Sr	1Zn1Pd	54.4	53.7	6.9	8.4	76.9	75.5
29	0.1Br	1Mg1Au	48.8	47.9	9.9	10.3	64.7	62.4
30	0.001Eu	2Pd2Au	56.1	55.6	7.8	8.7	75.4	75.9
31	0.1W	3Au2Zn	48.2	47.1	9.7	10.4	62.4	60.9
32	0.1Ni	1Mg4Pd	49.2	47.3	9.3	10.5	63.2	61.9
33*	—	—	50.3	44.3	9.8	18.3	77.9	55.7
34*	0.3Cr	—	46.2	42.4	14.5	16.9	68.3	57.5
35*	0.3La	—	46.1	42.7	14.5	18.8	66.2	58.3
36*	0.1Ca	7Mg	50.1	44.2	9.8	18.6	75.9	55.4
37*	0.1La	7Pd	47.6	44.5	12.4	16.9	56.5	54.8

[0037]As for the reflection film using the silver alloy of this invention, it turns out that it not only has a good initial characteristic, but CNR, a jitter, and a modulation factor hardly deteriorate also after high-humidity/temperature storage, but it can obtain a reliable disk so that clearly from Table 9. On the other hand, since an initial characteristic with a good disk of the samples 33-37 which are comparative examples is not acquired, or either CRN, a jitter and a modulation factor deteriorate greatly after keeping it with high-humidity/temperature, it turns out that sufficient reliability is not securable.

[0038]The above result shows that especially the Ag alloy of this invention is suitable as a reflection film of an optical disc as an object for the optical discs of the next generation called for from now on. Although the reflection film was produced by sputtering process in the above-mentioned example, it can create also by various membrane formation art, such as various vacuum deposition methods, the ion plating method, various CVD methods, and the plating method.

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(54) 【発明の名称】 光記録ディスク反射膜用銀合金

(57) 【要約】

【課題】 高い熱伝導性を有すると同時に、高いデータの信頼性を確保することができ、高記録密度対応の光記録ディスク用として好適な反射膜用銀合金を提供する。

【解決手段】 反射膜用銀合金は、Agを主成分とし、Cr、Zr、La、Ce、Eu、Ca、Sr、Ba、Ru、Ni、Wから選ばれた少なくとも1種の第1の添加元素を0.001～0.1重量%含んでいる。この反射膜用銀合金は、上記第1の添加元素に加え、Zn、Mg、Au、Pdから選ばれた少なくとも1種の第2の添加元素を0.1～5重量%含むことができる。

【特許請求の範囲】

【請求項1】 Agを主成分とし、Cr、Zr、La、Ce、Eu、Ca、Sr、Ba、Ru、Ni、Wからなる群から選ばれた少なくとも1種の添加元素を0.001～0.1重量%含み、残部が不可避不純物からなることを特徴とする光記録ディスク反射膜用銀合金。

【請求項2】 前記添加元素に加え、Zn、Mg、Au、Pdからなる群から選ばれた少なくとも1種の第2の添加元素を0.1～5重量%含むことを特徴とする、請求項1に記載の光記録ディスク反射膜用銀合金。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、各種光記録ディスクの反射膜として用いられる銀合金に関する。

【0002】

【従来の技術】コンピュータ情報や映像情報あるいは音楽情報を記録する媒体として、CD、CD-R、CD-RW、DVD、DVD-RW、DVD-RAM、MO、MD等の各種光記録ディスク（以下、光ディスクと云う）が用いられている。

【0003】これらの光ディスクは、方式によってそれぞれ構造は異なるものの、いずれもポリカーボネートのような透明なプラスチック製円盤を基板とし、その上に反射膜や保護膜等の各種機能を有する薄膜が層状に形成されている。

【0004】かかる光ディスクの反射膜は、記録の読み書きに使用するレーザー光を反射する機能と共に、レーザー光に起因する熱を逃す等の機能を有するものであり、いずれの方式の光ディスクにも用いられている。この反射膜の材質としては、主にAl、Au、Ag、又はこれらの合金が用いられている。

【0005】また、これらの反射膜は、Al、Au、Ag、又はこれらの合金からなるターゲットを用い、通常のスパッタリング法等により形成される。

【0006】

【発明が解決しようとする課題】近年、光ディスクの記録密度が向上するに伴って、熱伝導性の高い反射膜の要求が高まってきている。しかしながら、Alの反射膜については、熱伝導性が低い点から要求特性を満足できないことが明らかになっている。また、Auの反射膜は高熱伝導性に関する要求特性を満足できる可能性を有するが、価格が非常に高いことから、市販の光ディスクに用いることは困難である。

【0007】一方、Agの反射膜については、熱伝導性は満足するものの、データの書換えや高温高湿環境下での保管等による特性の劣化が大きく、データの信頼性を確保し難いという問題点を有している。このため、データの信頼性を確保しながら、同時に熱伝導性の要求特性を完全に満足する反射膜は得られていない。

【0008】本発明は、かかる従来の事情に鑑み、高い

データの信頼性を確保しながら、同時に高い熱伝導性を有し、高記録密度対応の光ディスク用として好適な反射膜用銀合金を提供することを目的とする。

【0009】

【課題を解決するための手段】上記目的を達成するため、本発明が提供する光記録ディスクの反射膜用銀合金は、Agを主成分とし、Cr、Zr、La、Ce、Eu、Ca、Sr、Ba、Ru、Ni、Wからなる群から選ばれた少なくとも1種の添加元素を0.001～0.1重量%含み、残部が不可避不純物からなることを特徴とする。

【0010】また、上記本発明の光記録ディスク反射膜用銀合金においては、前記添加元素に加え、更にZn、Mg、Au、Pdからなる群から選ばれた少なくとも1種の第2の添加元素を0.1～5重量%含むことができる。

【0011】

【発明の実施の形態】本発明者らは、従来の純Agからなる光ディスクの反射膜がデータの信頼性において劣る原因を種々検討した結果、結晶粒の粗大化ないしは膜の腐食に主な原因があることを確認し、その対策として各種元素の添加による合金化が有効であることを見出した。

【0012】即ち、本発明の光ディスクの反射膜用銀合金においては、主成分であるAgに対し、Cr、Zr、La、Ce、Eu、Ca、Sr、Ba、Ru、Ni、Wから選ばれた少なくとも1種の添加元素を0.001～0.1重量%含んでいる。これらの添加元素は、銀合金の耐熱性を向上させることによって反射膜中の結晶粒の粗大化を抑える働きをし、同時に結晶粒の微細化により高い反射率を安定的に得られるようになる。また、これらの添加元素を含むことによりターゲットの結晶粒径も微細化され、スパッタリングレートが均一化されるといった効果も得られる。

【0013】これらの元素の添加量を合計で0.001～0.1重量%としたのは、0.001重量%未満では濃度が低すぎて十分な添加効果が得られず、逆に0.1重量%を超えると合金の耐食性が低下し、書換えによるディスクの特性劣化が発生するからである。これらの添加元素は2種以上を組合わせて添加した場合にも所望の特性を達成することは可能であるが、一般的にはいずれか1種を単独で添加する方が得られる添加効果は大きくなる。

【0014】また、本発明の光ディスクの反射膜用銀合金における第2の形態として、上記の第1の添加元素に加えて、Zn、Mg、Au、Pdからなる群から選ばれた少なくとも1種の第2の添加元素を0.1～5重量%含むことができる。これら第2の添加元素は、耐食性を向上させる効果を有するものであり、特にZnSを含む保護膜を備える光ディスクの場合に有効である。

【0015】これら第2の添加元素の添加量を0.1～5重量%としたのは、0.1重量%未満では濃度が低すぎて耐食性向上の効果が十分でなく、逆に5重量%を超えると合金の熱伝導性が低下し、光ディスクの高記録密度化に対応できなくなるからである。

【0016】尚、本発明は反射膜を構成するAg合金の組成を規定したものであり、反射膜の形成に用いられるスパッタリングターゲットの組成についても同様に規定することができる。

【0017】また、本発明の反射膜は、光ディスク用の他にも、耐食性が要求され且つ高反射率が必要な反射鏡の反射膜、照明器具用の反射膜、標識用の反射膜、リフレクター用の反射膜等の用途、あるいは放熱性も重要となる液晶ディスプレイ（LCD）やプラズマディスプレ

イ（PDP）、エレクトロミネッセンス（EL）ディスプレイ等の反射膜のような用途、更には電気抵抗率が小さいことが必要な各種配線材料等の用途にも適用が可能である。

【0018】

【実施例】原料として99.9～99.999%の純度を有するAg、Cr、Zr、La、Ce、Eu、Ca、Sr、Ba、Ru、Ni、W、Zn、Mg、Au、Pdの塊又は粉末を用い、真空溶解炉を用いた溶解鋳造法ないしはホットプレスを用いた粉末冶金法により、各試料のターゲットを作製した。得られた各試料におけるターゲットの組成を下記表1に示す。

【0019】

【表1】

試料	ターゲット組成(wt%)		ターゲット組成(at%)
	第1添加元素	第2添加元素	
1	0.001Zr	—	Ag99.999Zr0.001
2	0.001Ce	—	Ag99.999Ce0.001
3	0.001Ca	—	Ag99.997Ca0.003
4	0.001Ru	—	Ag99.999Ru0.001
5	0.001Sr	—	Ag99.999Sr0.001
6	0.001Ba	—	Ag99.999Ba0.001
7	0.01Cr	—	Ag99.979Cr0.021
8	0.01La	—	Ag99.992La0.008
9	0.1Eu	—	Ag99.920Eu0.071
10	0.1Zr	—	Ag99.882Zr0.118
11	0.1Ce	—	Ag99.923Ce0.077
12	0.1Ca	—	Ag99.731Ca0.269
13	0.1Ru	—	Ag99.893Ru0.107
14	0.001Ni	—	Ag99.998Ni0.002
15	0.1Ni	—	Ag99.816Ni0.184
16	0.001W	—	Ag99.999W0.001
17	0.1W	—	Ag99.941W0.059
18	0.01Ru	0.5Zn	Ag99.167Ru0.011Zn0.823
19	0.01Ce	5Zr	Ag92.000Ce0.008Zn7.992
20	0.01Zr	0.5Mg	Ag97.807Zr0.012Mg2.181
21	0.01Ca	5Mg	Ag81.049Ca0.023Mg18.929
22	0.1Cr	0.5Au	Ag99.518Cr0.274Au0.208
23	0.001Cr	5Au	Ag97.198Cr0.002Au2.802
24	0.1La	0.5Pd	Ag99.415La0.078Pd0.507
25	0.001La	5Pd	Ag94.934La0.001Pd5.066
26	0.01W	5Au	Ag97.192W0.006Au2.802
27	0.01Ni	5Pd	Ag94.916Ni0.018Pd5.066
28	0.1Sr	1Zn1Pd	Ag97.239Sr0.122Zn1.638Pd1.001
29	0.1Br	1Mg1Au	Ag95.082Ba0.075Mg4.310Au0.532
30	0.001Eu	2Pd2Au	Ag96.849Eu0.001Pd2.046Au1.105
31	0.1W	3Au2Zn	Ag94.993W0.069Zn3.303Au1.645
32	0.1Ni	1Mg4Pd	Ag91.625Ni0.177Mg4.284Pd3.914
33*	—	—	Ag
34*	0.3Cr	—	Ag99.38Cr0.62
35*	0.3La	—	Ag99.922La0.078
36*	0.1Ca	7Mg	Ag74.773Ca0.217Mg25.01
37*	0.1La	7Pd	Ag92.832La0.078Pd7.090

（注）表中の*を付した試料は比較例である（以下同じ）。

【0020】これらの各ターゲットを用いて、マグネトロンスパッタリング法により、厚み3000Åの特性評価用の薄膜をガラス基板上に形成した。尚、形成した薄膜の組成が、使用したターゲット組成とほぼ同等であることは化学分析により確認した。

【0021】得られた薄膜を用いて、反射率、熱伝導率、結晶粒安定性を評価した。即ち、熱伝導率については、薄膜の熱伝導率を直接測定することが難しかったた

め、直流4端子法により測定した電気抵抗からWiedemann-Franz則を用いて計算することにより求め、その結果を下記表2に示した。また、反射率の測定は分光光度計により、波長400、650、780nmで行ない、その結果を表3に示した。

【0022】

【表2】

試料	反射膜	熱伝導率(W/m・K)
1	Ag99.999Zr0.001	293.30
2	Ag99.999Ca0.001	296.25
3	Ag99.997Cu0.003	295.24
4	Ag99.999Ru0.001	294.98
5	Ag99.999Sr0.001	296.95
6	Ag99.999Ba0.001	297.07
7	Ag99.979Cr0.021	294.03
8	Ag99.992La0.008	201.54
9	Ag99.929Eu0.071	273.75
10	Ag99.882Zr0.118	259.92
11	Ag99.923Ce0.077	285.01
12	Ag99.731Ca0.269	285.05
13	Ag99.893Ru0.107	273.71
14	Ag99.998Ni0.002	291.86
15	Ag99.816Ni0.184	249.02
16	Ag99.999W0.001	296.84
17	Ag99.941W0.059	290.59
18	Ag99.167Ru0.011Zn0.823	237.13
19	Ag92.000Ca0.008Zn7.992	96.74
20	Ag97.807Zr0.012Mg2.181	208.47
21	Ag81.049Ca0.023Mg18.929	72.43
22	Ag99.518Cr0.274Au0.208	229.44
23	Ag97.196Cr0.002Au2.802	203.74
24	Ag99.415La0.078Pd0.507	262.99
25	Ag94.934La0.001Pd5.066	156.16
26	Ag97.192W0.006Au2.802	205.62
27	Ag94.916Ni0.018Pd5.066	148.86
28	Ag97.239Sr0.122Zn1.638Pd1.001	183.63
29	Ag95.082Ba0.076Mg4.310Au0.532	165.14
30	Ag96.849Eu0.001Pd2.045Au1.105	192.70
31	Ag94.993W0.059Zn3.303Au1.645	139.81
32	Ag91.625Ni0.177Mg4.284Pd3.914	107.83
33*	Ag	297.55
34*	Ag99.38Cr0.62	169.10
35*	Ag99.922La0.078	285.72
36*	Ag74.773Ca0.217Mg25.01	58.14
37*	Ag92.832La0.078Pd7.090	129.21

【0023】

【表3】

試料	反射率	反射率(%)		
		780(nm)	650(nm)	400(nm)
1	Ag99.999Zr0.001	97.9	97.7	94.2
2	Ag99.999Ce0.001	97.9	97.7	94.2
3	Ag99.997Cu0.003	97.9	97.7	94.2
4	Ag99.999Ru0.001	97.9	97.7	94.2
5	Ag99.999Sr0.001	97.9	97.7	94.2
6	Ag99.999Ba0.001	98.0	97.9	94.8
7	Ag99.979Cr0.021	97.5	97.3	94.5
8	Ag99.992La0.008	98.0	97.9	94.8
9	Ag99.929Eu0.071	98.0	97.9	94.8
10	Ag99.882Zr0.118	97.4	97.2	94.6
11	Ag99.923Ce0.077	98.0	97.9	94.8
12	Ag99.731Cu0.269	97.3	97.0	94.0
13	Ag99.893Ru0.107	97.4	97.1	94.0
14	Ag99.998Ni0.002	98.0	97.9	94.8
15	Ag99.816Ni0.184	97.9	97.7	94.3
16	Ag99.999W0.001	98.0	97.9	94.8
17	Ag99.941W0.059	98.0	97.9	94.8
18	Ag99.167Ru0.011Zn0.823	97.3	97.0	93.9
19	Ag92.000Ce0.008Zn7.992	90.2	89.9	85.9
20	Ag97.807Zr0.012Mg2.181	92.1	91.7	88.8
21	Ag81.049Ca0.023Mg18.929	80.9	79.0	65.3
22	Ag99.518Cr0.274Au0.208	97.4	97.2	94.4
23	Ag97.196Cr0.002Au2.802	91.9	90.1	88.2
24	Ag99.415La0.078Pd0.507	97.4	97.2	94.3
25	Ag94.934La0.001Pd5.066	90.3	89.9	86.0
26	Ag97.192W0.006Au2.802	91.8	90.2	88.3
27	Ag94.916Ni0.018Pd5.066	90.8	89.9	86.2
28	Ag97.239Sr0.122Zn1.638Pd1.001	91.6	90.1	88.5
29	Ag95.082Ba0.076Mg4.310Au0.532	90.7	89.9	86.1
30	Ag96.849Eu0.001Pd2.045Au1.105	91.3	89.8	88.3
31	Ag94.993W0.059Zn3.903Au1.645	90.2	90.8	85.7
32	Ag91.625Ni0.177Mg4.284Pd3.914	90.2	89.7	85.7
33*	Ag	98.0	97.9	94.8
34*	Ag99.38Cr0.62	97.5	97.2	94.1
35*	Ag99.922La0.078	98.0	97.9	94.8
36*	Ag74.773Ca0.217Mg25.01	74.9	71.3	63.4
37*	Ag92.832La0.078Pd7.090	91.2	89.9	87.8

【0024】また、結晶粒の粗大化の起こり難さを表わす指標として、高真空中にて150℃で48時間の熱処理を施した前後の結晶粒径の変化を調査した。熱処理前後の結晶粒径として、X線回折ピークの半値幅から求めた計算値を下記表4に、及び原子間力顕微鏡により測定

した表面粗さ(中心線表面粗さR_a)によって評価した結果を下記表5に示した。尚、表5の場合、表面粗さが大きいほど、結晶粒径が大きいと考えられる。

【0025】

【表4】

試料	反射膜	粒径 L (111) [Å]	
		熱処理前	熱処理後
1	Ag99.999Zr0.001	175	170
2	Ag99.999Ce0.001	174	171
3	Ag99.997Ca0.003	176	170
4	Ag99.999Ru0.001	175	170
5	Ag99.999Sr0.001	175	171
6	Ag99.999Ba0.001	175	170
7	Ag99.979Cr0.021	176	173
8	Ag99.992La0.008	176	170
9	Ag99.929Eu0.071	175	170
10	Ag99.882Zr0.118	173	170
11	Ag99.923Ce0.077	174	170
12	Ag99.731Ca0.269	175	170
13	Ag99.893Ru0.107	175	170
14	Ag99.998Ni0.002	176	171
15	Ag99.816Ni0.184	175	170
16	Ag99.999W0.001	174	170
17	Ag99.941W0.059	175	170
18	Ag99.167Ru0.011Zn0.823	155	151
19	Ag92.000Ce0.008Zn7.992	155	155
20	Ag97.807Zr0.012Mg2.181	170	170
21	Ag81.049Ca0.023Mg18.929	170	170
22	Ag99.518Cr0.274Au0.208	160	160
23	Ag97.196Cr0.002Au2.802	160	160
24	Ag99.415La0.078Pd0.507	165	165
25	Ag94.934La0.001Pd5.066	165	165
26	Ag97.192W0.006Au2.802	160	160
27	Ag94.916Ni0.018Pd5.066	165	165
28	Ag97.239Sr0.122Zn1.638Pd1.001	150	150
29	Ag95.082Ba0.076Mg4.310Au0.582	150	150
30	Ag96.849Eu0.001Pd2.045Au1.105	145	145
31	Ag94.993W0.059Zn3.303Au1.645	145	145
32	Ag91.625Ni0.177Mg4.284Pd3.914	145	145
33*	Ag	165	175
34*	Ag99.38Cr0.62	175	193
35*	Ag99.922La0.078	175	180
36*	Ag74.773Cu0.217Mg25.01	165	165
37*	Ag92.832La0.078Pd7.090	165	165

【0026】

【表5】

試料	反射膜	表面電阻 R_a (Ω)	
		熱処理前	熱処理後
1	Ag99.999Zr0.001	<10	<10
2	Ag99.999Ce0.001	<10	<10
3	Ag99.997Ca0.003	<10	<10
4	Ag99.999Ru0.001	<10	<10
5	Ag99.999Sr0.001	<10	<10
6	Ag99.999Ba0.001	<10	<10
7	Ag99.979Cr0.021	<10	<10
8	Ag99.992La0.008	<10	<10
9	Ag99.929Eu0.071	<10	<10
10	Ag99.882Zr0.118	<10	<10
11	Ag99.928Ce0.077	<10	<10
12	Ag99.731Ca0.269	<10	<10
13	Ag99.893Ru0.107	<10	<10
14	Ag99.998Ni0.002	<10	<10
15	Ag99.816Ni0.184	<10	<10
16	Ag99.999W0.001	<10	<10
17	Ag99.941W0.059	<10	<10
18	Ag99.167Ru0.011Zn0.823	<10	<10
19	Ag92.000Ce0.008Zn7.992	<10	<10
20	Ag97.807Zr0.012Mg2.181	<10	<10
21	Ag81.049Ca0.023Mg18.929	<10	<10
22	Ag99.518Cr0.274Au0.208	<10	<10
23	Ag97.196Cr0.002Au2.802	<10	<10
24	Ag99.415La0.078Pd0.507	<10	<10
25	Ag94.934La0.001Pd5.066	<10	<10
26	Ag97.192W0.006Au2.802	<10	<10
27	Ag94.916Ni0.018Pd5.066	<10	<10
28	Ag97.239Sr0.122Zn1.638Pd1.001	<10	<10
29	Ag95.082Ba0.076Mg4.910Au0.532	<10	<10
30	Ag96.849Eu0.001Pd2.045Au1.105	<10	<10
31	Ag94.993W0.059Zn3.303Au1.645	<10	<10
32	Ag91.625Ni0.177Mg4.284Pd3.914	<10	<10
33*	Ag	<10	23
34*	Ag99.38Cr0.62	10	11
35*	Ag99.922La0.078	10	10
36*	Ag74.773Ca0.217Mg25.01	<10	10
37*	Ag92.832La0.078Pd7.000	<10	10

【0027】以上の結果から、本発明の銀合金を用いることにより、反射率と熱伝導率が高く、しかも熱を受けても結晶粒の粗大化が起こり難い、優れた特性の反射膜を得られることが分かる。

【0028】次に、本発明の反射膜を光ディスクに用いた場合のディスク特性を評価した。即ち、基板1として厚さ1.2mm、直径120mm、溝（トラック）ピッチ1.6 μ m、溝深さ50nmのCD用基板と、基板2として厚さ0.6mm、直径120mm、溝ピッチ0.8 μ m、溝深さ35nmのDVD用基板の、2種類のポリカーボネイト製基板を用いた。

【0029】CD用評価ディスクは、上記基板1上にスパッタリングにより下部保護膜、記録膜、上部保護膜、

拡散防止膜、反射膜を順次形成した後、紫外線硬化樹脂のオーバーコート層を5 μ mの厚みに形成することにより得た。また、DVD用評価ディスクは、上記基板2上に同様に、下部保護膜、記録膜、上部保護膜、拡散防止膜、反射膜、及び厚み4 μ mのオーバーコート層を順次形成した後、その上に厚さ0.6mm、直径120mmのポリカーボネイト基板を紫外線硬化樹脂で貼り合わせるによって作製した。上記の各膜の材料と共に、膜形成に用いたスパッタリング条件を下記表6に、作製した各ディスク試料の構成を下記表7に、及び各膜の厚みを下記表8に示した。

【0030】

【表6】

膜	材料系	投入電力 (kW)	ガス圧 (mTorr)	その他の条件
保護膜	ZnS+SiO ₂ 系	RF4.0	6	
拡散防止膜	SiNx	DC2.0	3	Siターゲット使用 N ₂ との反応スパッタ
	Ta ₂ O ₅	RF4.0	6	
	ZrO ₂	RF4.0	6	
	AlN	RF4.0	6	
	SiC	RF4.0	6	
記録膜	AgInSbTe系	DC0.5	3	
反射膜	Ag合金	DC1.0	3	

【0031】

【表7】

試料	反射膜	保護膜	抗酸防止膜	基板
1	Ag99.999Zr0.001	(ZnS)80(SiO ₂)20	AIN	1
2	Ag99.999Ce0.001	(ZnS)80(SiO ₂)20	AIN	1
3	Ag99.997Ca0.003	(ZnS)80(SiO ₂)20	AIN	2
4	Ag99.999Ru0.001	(ZnS)80(SiO ₂)20	AIN	1
5	Ag99.999Sr0.001	(ZnS)80(SiO ₂)20	AIN	2
6	Ag99.999Ba0.001	(ZnS)80(SiO ₂)20	AIN	1
7	Ag99.979Cr0.021	(ZnS)80(SiO ₂)20	AIN	2
8	Ag99.992La0.008	(ZnS)80(SiO ₂)20	AIN	2
9	Ag99.929Eu0.071	(ZnS)80(SiO ₂)20	AIN	2
10	Ag99.982Zr0.118	(ZnS)80(SiO ₂)20	SiC	1
11	Ag99.923Ce0.077	(ZnS)80(SiO ₂)20	SiC	1
12	Ag99.731Cu0.269	(ZnS)80(SiO ₂)20	SiC	1
13	Ag99.893Ru0.107	(ZnS)80(SiO ₂)20	SiC	2
14	Ag99.998Ni0.002	(ZnS)80(SiO ₂)20	SiC	2
15	Ag99.816Ni0.184	(ZnS)80(SiO ₂)20	SiC	1
16	Ag99.999W0.001	(ZnS)80(SiO ₂)20	SiC	1
17	Ag99.941W0.059	(ZnS)80(SiO ₂)20	SiC	1
18	Ag99.167Ru0.011Zn0.823	(ZnS)80(SiO ₂)20	S:Nx	2
19	Ag92.000Ce0.008Zn7.992	(ZnS)80(SiO ₂)20	-	2
20	Ag97.807Zr0.012Mg2.181	(ZnS)80(SiO ₂)20	Ta ₂ O ₅	2
21	Ag81.049Cu0.023Mg18.929	(ZnS)80(SiO ₂)20	-	2
22	Ag99.518Cr0.274Au0.208	(ZnS)80(SiO ₂)20	AIN	1
23	Ag97.196Cr0.002Au2.802	(ZnS)80(SiO ₂)20	SiNx	1
24	Ag99.415La0.078Pd0.507	(ZnS)80(SiO ₂)20	ZrO ₂	1
25	Ag94.934La0.001Pd5.066	(ZnS)80(SiO ₂)20	-	2
26	Ag97.192W0.006Au2.802	(ZnS)80(SiO ₂)20	-	2
27	Ag94.916Ni0.018Pd5.066	(ZnS)80(SiO ₂)20	-	2
28	Ag97.239Sr0.122Zn1.638Pd1.001	(ZnS)80(SiO ₂)20	-	1
29	Ag95.082Ba0.076Mg4.310Au0.532	(ZnS)80(SiO ₂)20	-	2
30	Ag96.849Eu0.001Pd2.045Au1.105	(ZnS)80(SiO ₂)20	-	1
31	Ag94.993W0.059Zn9.303Au1.646	(ZnS)80(SiO ₂)20	-	2
32	Ag91.625Ni0.177Mg4.284Pd3.914	(ZnS)80(SiO ₂)20	-	2
33*	Ag	(ZnS)80(SiO ₂)20	SiNx	1
34*	Ag99.38Cr0.62	(ZnS)80(SiO ₂)20	Ta ₂ O ₅	2
35*	Ag99.922La0.078	(ZnS)80(SiO ₂)20	SiC	2
36*	Ag74.773Cu0.217Mg25.01	(ZnS)80(SiO ₂)20	-	1
37*	Ag92.832La0.078Pd7.090	(ZnS)80(SiO ₂)20	-	2

【0032】

【表8】

試料	下部保護膜 (nm)	記録膜 (nm)	上部保護膜 (nm)	拡散防止膜 (nm)	反射膜 (nm)
1	85	17.5	35	5	100
2	85	17.5	34	5	100
3	80	17.0	25	5	160
4	85	17.5	35	5	120
5	80	17.0	25	5	160
6	87	17.5	34	5	120
7	79	17.0	25	5	160
8	80	17.0	26	5	160
9	81	17.0	26	5	160
10	84	17.5	35	5	100
11	86	17.5	34	5	120
12	85	17.5	35	5	100
13	80	17.0	25	5	160
14	80	17.0	25	5	160
15	84	17.5	36	5	100
16	85	17.5	34	5	100
17	85	17.5	34	5	100
18	80	17.0	25	5	170
19	80	17.0	25	—	170
20	80	17.0	25	5	170
21	80	17.0	25	—	160
22	85	17.5	35	5	100
23	85	17.5	34	5	120
24	85	17.5	34	5	110
25	80	17.0	25	—	160
26	80	17.0	25	—	160
27	80	17.0	25	—	160
28	85	17.5	34	—	100
29	80	17.0	25	—	160
30	85	17.5	34	—	100
31	80	17.0	25	—	160
32	80	17.0	25	—	160
33*	85	17.5	34	5	110
34*	79	17.0	27	5	170
35*	80	17.0	25	5	160
36*	85	17.5	35	—	100
37*	80	17.0	25	—	160

【0033】以上の様にして得た各ディスクの評価として、キャリア対ノイズ比(CNR)、ジッター、変調度を測定した。CD用評価ディスクの場合は、波長780nmのレーザー光をNA0.55のレンズを通して1μmのスポット径に絞って照射することにより測定した。線速は2.0、5.0、10.0m/secの3水準とした。また、DVD用評価ディスクの場合は、波長633nmのレーザー光をNA0.6のレンズを通して0.5μmのスポット径に絞って照射することにより測定した。線速は7.0、15.0m/secの2水準とした。

【0034】いずれの場合も、各線速でレーザーパワー(Pe:消去用パワー、Pw:書き込み用パワー)をP

e、Pw=0.5に固定し、Pwを8~16mWと変化させた場合に、CNRが大きく且つジッターが小さくなる条件を選択して測定を行った。読み取りのレーザーパワーは0.9mWを用いた。尚、製膜後の記録膜は非晶質であったが、10mWのDC光によりディスク全面を結晶化させた状態で試験に供している。

【0035】更に、ディスクの信頼性を確認する目的で、80℃85%RHの高温高湿槽に500時間保管した後、ディスク特性の測定を上記と同様に行った。高温高湿保管の前及び後におけるディスク特性、即ちCNR、ジッター、変調度の測定結果を下記表9に示した。

【0036】

【表9】

試料	反射膜組成(wt%)		ディスク特性					
	第1添加 元素	第2添加 元素	CNR(dB)		ジッター(%)		変調度(%)	
			前	後	前	後	前	後
1	0.001Zr	—	56.1	54.3	6.7	8.4	73.2	70.3
2	0.001Ce	—	56.0	54.8	6.9	8.3	72.1	69.3
3	0.001Ca	—	49.3	48.7	9.2	10.4	65.7	64.9
4	0.001Ru	—	54.3	53.8	6.6	8.4	69.2	69.0
5	0.001Sr	—	49.5	48.0	9.3	10.6	62.7	61.9
6	0.001Ba	—	54.8	54.0	7.1	8.0	71.3	70.1
7	0.01Cr	—	49.5	48.3	9.5	10.6	63.8	61.8
8	0.01La	—	49.2	48.1	10.3	11.2	64.3	62.0
9	0.1Eu	—	48.6	47.9	10.2	11.3	62.6	61.9
10	0.1Zr	—	56.2	54.9	7.7	8.9	68.2	66.3
11	0.1Ce	—	54.6	53.8	7.5	8.8	70.2	68.5
12	0.1Ca	—	53.0	52.6	7.4	8.5	68.5	67.2
13	0.1Ru	—	49.1	47.5	9.9	10.7	61.7	61.6
14	0.001Ni	—	49.5	48.2	10.4	11.3	63.9	61.3
15	0.1Ni	—	49.9	49.4	7.3	8.7	69.4	67.6
16	0.001W	—	56.9	54.9	6.9	8.1	72.7	70.0
17	0.1W	—	56.8	54.7	6.9	8.4	70.1	69.4
18	0.01Ru	0.5Zn	49.4	49.5	9.2	10.4	65.7	64.9
19	0.01Ce	5Zn	49.5	49.3	9.4	10.4	67.6	68.2
20	0.01Zr	0.6Mg	49.7	49.5	9.8	10.8	68.2	68.7
21	0.01Ca	5Mg	48.6	48.3	10.5	11.4	64.6	65.3
22	0.1Cr	0.5Au	55.1	53.9	6.9	8.1	74.4	74.3
23	0.001Cr	5Au	54.9	54.8	6.9	8.4	69.8	69.4
24	0.1La	0.6Pd	56.2	55.8	7.3	8.5	77.6	77.5
25	0.001La	5Pd	49.9	59.7	10.3	11.2	65.8	66.2
26	0.01W	5Au	50.1	49.9	10.3	11.2	66.5	66.9
27	0.01Ni	5Pd	50.0	49.6	9.2	10.4	73.7	76.9
28	0.1Sr	1Zn1Pd	54.4	63.7	6.9	8.4	76.9	75.5
29	0.1Br	1Mg1Au	48.8	47.9	9.9	10.3	64.7	62.4
30	0.001Eu	2Pd2Au	56.1	55.6	7.8	8.7	75.4	75.9
31	0.1W	3Au2Zn	48.2	47.1	9.7	10.4	62.4	60.9
32	0.1Ni	1Mg4Pd	49.2	47.3	9.3	10.5	63.2	61.9
33*	—	—	50.3	44.3	9.8	18.3	77.9	56.7
34*	0.3Cr	—	46.2	42.4	14.5	16.9	66.3	57.5
35*	0.3La	—	46.1	42.7	14.5	18.8	66.2	58.3
36*	0.1Cu	7Mg	50.1	44.2	9.8	18.6	75.9	56.4
37*	0.1La	7Pd	47.6	44.5	12.4	16.9	56.5	54.8

【0037】表9から明らかなように、本発明の銀合金を用いた反射膜は、良好な初期特性を有するばかりでなく、高温高湿保管後にもCNR、ジッター、変調度が殆ど劣化せず、信頼性の高いディスクを得られることが分かる。一方、比較例である試料33～37のディスクは、良好な初期特性が得られないか、若しくは高温高湿での保管後にCNR、ジッター及び変調度のいずれかが大きく劣化するため、十分な信頼性を確保できないことが分かる。

【0038】以上の結果から、本発明のAg合金は光ディスクの反射膜として、特に今後求められる次世代の光

ディスク用として好適であることが分かる。尚、上記実施例ではスパッタリング法により反射膜を製膜したが、種々の真空蒸着法、イオンプレーティング法、各種CVD法、及びめっき法などの各種成膜技術によっても作成することができる。

【0039】

【発明の効果】本発明によれば、高い熱伝導性を有すると同時に、高いデータの信頼性を確保することができ、高記録密度対応の光記録ディスク用として好適な反射膜用銀合金を提供することができる。

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